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Effects of Phosphorus Doping Concentration in a SiC Thin Film Coated Electrode on Water Electrolysis Electrode

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1. Introduction

Water splitting is one of the method of hydrogen generation, which is a clean generation method without CO_2 emission. Recently, it has been reported a water splitting method using photoelectrodes with semiconductor materials by using solar light[1]. Among them, silicon carbide (SiC) is a chemically stable and a wide bandgap, which possesses excellent photo-electrode properties[2]. On the other hand, in principle, the photoelectrode is inefficient in a water splitting. Wherein, we focused on a SiC thin film coating on a base metal for a water splitting electrode.

In order to deposit a low resistivity SiC film on a base metal, it is necessary to impurity doping at low temperature growth. We have been reported the growth of high quality SiC thin film on Si and base metal substrates at low temperature by chemical vapor deposition (CVD) method using vinylsilane as a novel single source precursor [3]. The results support the SiC film formed using vinylsilane is promising material for metal electrode coating. Moreover, we also reported *in-situ* phosphorus (P) doping to poly-crystalline 3C-SiC using tri-ethyl-phosphorus (TEP) as a P source[4].

However, the electrode properties of SiC thin film for a water splitting has not been clarified yet. Therefore, in this work, we investigated the electrode properties of *in-situ* P doping SiC thin film grown on a low-resistivity Si substrate using vinylsilane precursor and PF_3 doping gas.

2. Experimental methods

The SiC thin films were grown on n-type low- and high-resistivity ($\leqq$0.02 and $\geqq$1000 Ωcm) Si (100) substrates by a cold-wall thermal CVD using vinylsilane, PF_3, and Ar gas as a precursor, doping gas, and carrier gas, respectively. The flow rate of vinylsilane and PF_3 gas was 5 and 3.5 to 69 sccm, respectively. The growth pressure and growth temperature were 12 Pa and 820-910 °C, respectively.

The film thickness of SiC thin film was evaluated by scanning electron microscope (SEM). The chemical bonding of SiC film was analyzed by Fourier transform-infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). The electrochemical characteristics in the SiC thin film was examined by cyclic voltammetry with Pt plate and Ag/AgCl electrodes as counter electrode and reference electrode in the electrolyte of KCl with 1 mol/l (pH7) by the three-electrode system. The carrier density in the SiC thin films was evaluated by using capacitance-voltage (C-V) measurement by a two-electrode system.

3. Result and discussion

Figure 1 shows the cross sectional SEM image of the SiC thin film on Si substrate. The film thickness is estimated to be 80 nm. The thickness of other samples is a range of 50 to 200 nm. Figure 2 shows the absorbance spectra of SiC thin films grown with various PF_3 flow rate. The peak at around 800 cm^{-1} is observed from all sample, which is attributed to Si-C bond[5]. The peak position hardly changes with increasing PF_3 gas flow rate. It means that introducing PF_3 gas mixing to vinylsilane precursor hardly affects the bonding state of Si-C in the SiC thin films. And then, in order to conform P atoms in to the SiC thin film, we measured P 2p, Si 2p, and C1s spectra by using XPS.

Figure 3 shows the P composition ratio from the Si 2p and C 1s and resistivity in the SiC thin film as a function of PF_3 gas flow rate. The P composition ratio increases with increasing PF_3 gas flow rate. The resistivity was evaluated by using the films thickness from the SEM images and the results of four-point probe method. The resistivity of SiC thin films decreases with increasing the PF_3 gas flow rate. These results mean that the P composition ratio in the SiC thin film can be controlled by PF_3 gas flow rate.

Figure 4 shows Motto-Schottky plots in the SiC/Si electrode with different PF_3 gas flow rate using result of C-V measurement with two terminal method. We calculated ionized donor concentration (N_D^+) of the SiC thin films grown with various PF_3 flow rate from the slope of Motto-Schottky plots by capacitance-voltage measurement.

The N_D^+ and resistivity in the SiC thin film are summarized with the values of previously reported[4,6-7] as shown in Fig.5. Nevertheless, the SiC thin film is an amorphous structure, the values of resistivity in this work are close to that of 3C-SiC crystal structure in the same donor concentration region. Thus, the SiC thin film is promising material as an electrode. Next, we evaluated an electrode performance of the SiC thin film.

Figure 6 shows the result of cyclic voltammogram in the SiC thin films on low-resistivity Si substrate (SiC/Si electrode) grown with various PF_3 flow rate. For comparison, the result of low-resistivity Si substrate as Si electrode is also shown in Fig.6. The current of all samples increases with increasing

negative voltage. This current direction indicates to occur in connection with hydrogen generation. Here, we defined that threshold voltage (V_{th}) is the current density at 1.0 mA/cm^2. The V_{th} in the SiC/Si electrode with PF_3 gas 14 sccm flows is -1.49 V, which is lower than that in the Si electrode (-1.85 V). Besides, the V_{th} has no relationship to the increasing PF_3 gas flow rate (not shown). We investigated the relationship between V_{th} and ionized donor concentration (N_D^+) in the SiC thin film.

Figure 7 shows V_{th} as a function of N_D^+ and E_c-E_F. The V_{th} decrease with increasing N_D^+, which behaver like a convex parabolic characteristic. Here, we assumed that the condition of KCl side is same with different electrodes. It is considered interface properties of the n-SiC film and the KCl electrolyte in like a Schottky barrier diode. The lower N_D^+ of the SiC thin film, become lower the built-in potential (V_{bi}) value. As a result, the lower V_{bi} causes that a diffusion current easily flows. In contrast, the high N_D^+ sample is the lowest value in all sample in spite of highest V_{bi} value. The depletion layer width in this sample is 1.5 nm at 0 V. It is considered that dominant current mechanism is the tunnel current. We found that V_{th} can be controlled tuning of N_D^+, which is result in high efficiency for water electrolysis.

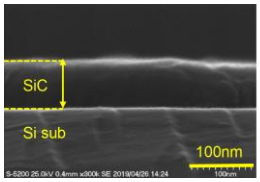

Fig. 1 The cross sectional SEM image of the SiC thin films.

4. Conclusions

We investigated effects of phosphorus doping concentration in SiC thin film coating electrode on water electrolysis electrode. We have successfully decrease in resistivity of the SiC thin films with precursor vinylsilane and doping gas PF_3 by using thermal CVD. In addition, we indicated the SiC thin films for water electrolysis electrode is different from V_{th} with various PF_3 gas. We investigated that relationship between the V_{th} and N_D^+. We succeeded in lowering the V_{th} by adjusting N_D^+ lower or higher. Based on these result, we demonstrated that the *in-situ* P doped SiC electrode by the precursor vinylsilane and the doping PF_3 is usefulness as improving efficiency in water electrolysis.

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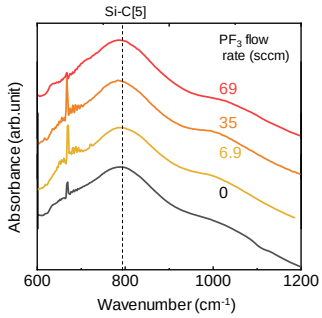

Fig. 2 Absorbance spectra of SiC thin film grown with various PF_3 flow rate.

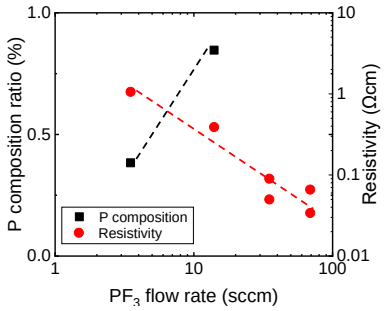

Fig. 3 P composition for Si and C composition and the resistivity in SiC thin film as a function of PF_3

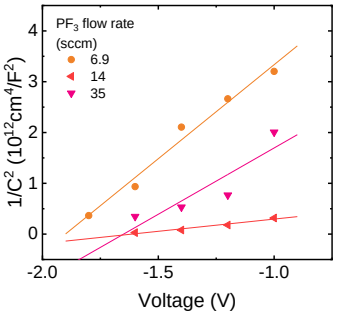

Fig. 4 Motto-Schottky plots in the SiC thin films grown with PF_3 flow rate.

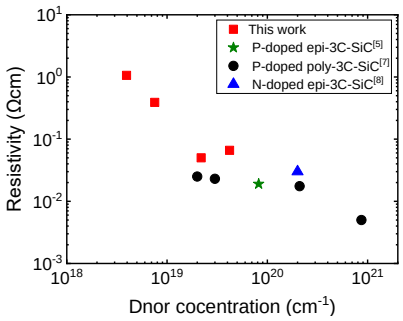

Fig. 5 The resistivity as a function donor concentration with the previously reported.

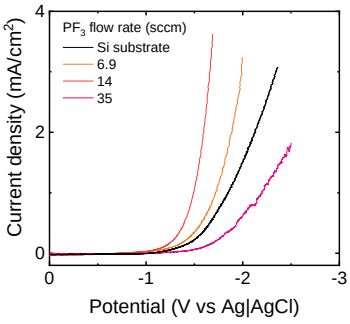

Fig. 6 Cyclic voltammogram in SiC thin films grown with various PF_3 flow rate.

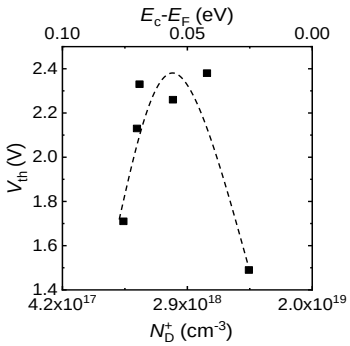

Fig. 7 V_{th} as a function N_D^+ and E_C-E_F in the SiC thin films.